

VII.I.4 Effect of Fuel and Air Impurities on PEM Fuel Cell Performance

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Projected End Date: Project continuation and direction determined annually by DOE

Objectives

- Evaluate the effects of fuel and air impurities on fuel cell (FC) performance
- Evaluate catalyst durability under the effects of impurities
- Investigate effect of impurities on FC components other than the membrane electrode assembly (MEA)
- Find ways to mitigate negative effects of impurities
- Demonstrate a method for cleaning sulfur poisoned Pt catalysts
- Quantify threshold levels of impurities

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan (HFCIT MYRDDP):

- A. Durability
- B. Cost
- C. Electrode Performance

Technical Targets

Targets for FC durability and impurity tolerance have not yet been established, mainly because of the lack of sufficient data concerning a rather large number of potential impurities both in the fuel and in the air.

However, during the rest of the fiscal year we will carry out the first durability tests with a hydrogen fuel mixture with composition specified to provide long-term FC operation without adverse degradation. The following table lists a first draft specification of hydrogen quality required as input into the fuel cell system. (Fuel Cells section of the MYRDDP, p. 8)

Table 3.4.16 Hydrogen Quality

Component	Level
Hydrogen	>99.9
Sulfur	10 ppb
CO	0.1 ppm
CO ₂	5 ppm

Table 3.4.16 Hydrogen Quality (Continued)

Component	Level
NH ₃	1 ppm
Non-Methane Hydrocarbons on a C1 basis	100 ppm
Particulates Conforming to ISO 14687	Not included in test

Approach

- Study the effects of air impurities on cathode performance (e.g. SO₂, NO₂).
- Determine the harmful threshold levels of SO₂ and NO₂ on FC performance.
- Identify materials or devices able to mitigate negative effects of impurities.
- Examine the effect of SO₂ on performance with dry and humidified air.
- Test tolerance of Pt-alloys to poisoning with H₂S.
- Test methods for reactivating sulfur-poisoned (e.g. H₂S and SO₂) Pt catalysts.

Accomplishments

- Determined the threshold harmful level of SO₂ is between 0.1 and 0.25 ppm.
- Established that the negative effect of H₂S and SO₂ on performance is due to surface Pt-catalyst poisoning.
- Demonstrated a simple and efficient electrochemical procedure for cleaning electrodes poisoned with H₂S and SO₂, with minimum FC operation interruption. The method consists of applying a current–voltage pulse with an external power source.
- Found out that Pt-Cu/C catalyst is not tolerant to 3 ppm H₂S.
- Determined that cathode contamination with NaCl affects mostly MEA protonic conductivity.

Future Directions

- Evaluate FC performance with the fuel mixture specified in Table 3.4.16.
- Investigate potential synergistic effects of impurities.
- Analyze the effects of other cations (besides Na⁺).
- In general, determine effects of ionic species in FC performance. Some ions may be corrosion products of system components (e.g. metal tubing).
- Elucidate the FC degradation mechanism produced by NO₂.
- Determine threshold levels for H₂S, CO₂, ethylene and NH₃ as fuel impurities.

Introduction

Proton exchange membrane fuel cells (PEMFCs) are devices that generate electrical power from two complementary electrochemical reactions. Hydrogen is oxidized at the anode and oxygen (from air) is reduced at the cathode. Thus, efficient fuel cell operation relies on the availability of both the cleanest fuel and air possible. These reactions take place on the surface of highly dispersed Pt catalysts

that are imbibed in a proton conducting ionomer within the catalyst layer. It has been shown that the catalytic activity of the Pt surface and proton conductivity of the ionomeric component is very sensitive to the presence of certain impurities.

In the hydrogen fuel, the impurities can be present in the primary source of fuel or can be generated during the reforming process. For instance, reformation of hydrocarbon fuels such as methane or gasoline, besides H₂, may produce

various impurities at levels that can be detrimental to FC operation. Typical fuel impurities are carbon monoxide (CO), ammonia (NH₃) and hydrogen sulfide (H₂S) [1-3]. On the other hand, ambient air contains pollutants (e.g. NO_x and SO₂), mostly coming from fossil fuel combustion, which also degrade FC performance [4-6]. In general, our project focuses on assessing the severity of the impurity effects and finding ways of mitigating their negative effects on performance.

Approach

In this period, we have focused our effort on the effects of H₂S, SO₂ and NaCl on performance. The tests have included a range of impurity concentrations at various operating conditions and times of exposure. These sulfur-compound impurities severely degrade FC performance; however, the maximum tolerance levels have not been determined yet. We have conducted tests aiming to establish these levels. This information is particularly useful in defining future fuel quality standards in industrial production of H₂ for fuel cells. H₂S and SO₂ degrading effects are not only severe but also irreversible due to Pt-catalyst poisoning. The most frequently recommended approach for mitigating their effects is gas filtration [5]. However, if the electrodes become inadvertently contaminated, a procedure for catalyst reactivation is needed. Here we describe a simple method for addressing this problem.

Results

The quantitative effect of a given impurity on performance depends on its concentration, time of exposure and operating conditions. Under a given set of conditions, it is important to establish the maximum concentration impurity that will not affect performance during a given period of time. Figure 1 shows the response of cell voltage with time for a series of constant current tests for different concentrations of SO₂ in the air stream. In each case the cathode was exposed to a total amount of 0.010 mol of SO₂. For this exposure, the threshold concentration is between 0.10 and 0.25 ppm. Cyclic voltammograms (CV) shown in Figure 2 indicate that performance degradation is due to catalyst poisoning. The decrease of H-desorption peaks and the

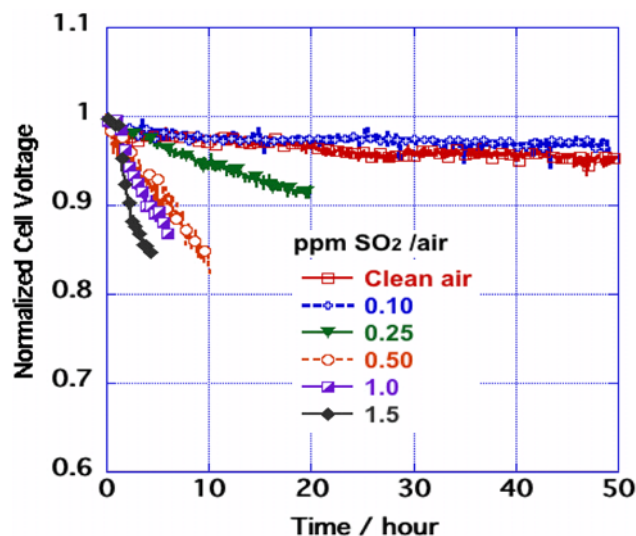


Figure 1. Effect of SO₂ Concentration on Cathode Performance at 80 °C (A total of 0.010 mmol of SO₂ was injected at the cathode at each concentration. Cell size: 50 cm²; anode and cathode loadings (mg Pt/cm²): 0.21 and 0.22 respectively. Cell run at 0.6 A/cm² constant current.)

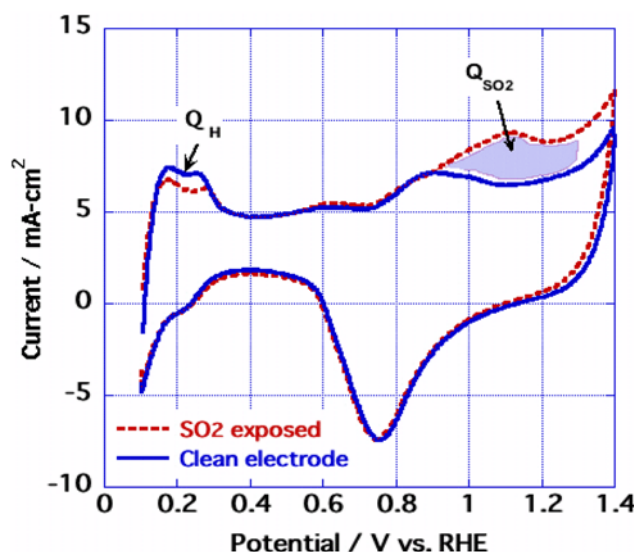


Figure 2. CVs of a Cathode Electrode Exposed to 1.5 ppm SO₂ for 4.3 hr at 80 °C (The CV of the clean electrode is also shown for comparison. Cell size: 50 cm²; anode and cathode loadings (mg Pt/cm²): 0.21 and 0.22 respectively. Scan rate: 50 mV/s.)

increased anodic waves between 0.9-1.3 V reveal S-species strongly adsorbed on the cathode Pt surface.

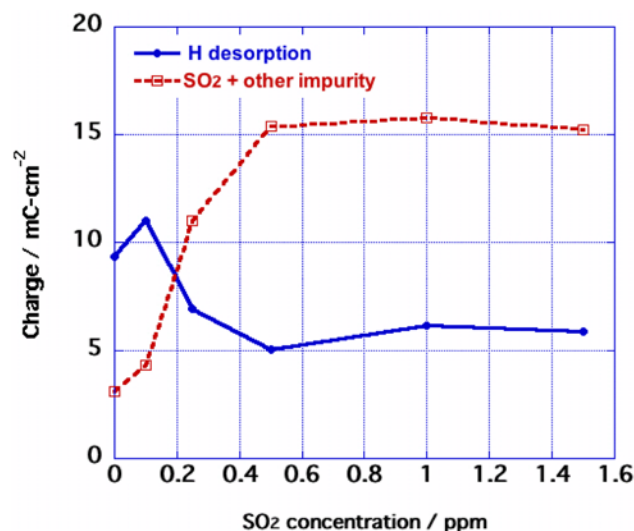


Figure 3. Charge Variation for H-desorption and for SO₂ Oxidation as a function of SO₂ Concentration (Values calculated from CVs as shown in Figure 2.)

The corresponding electric charges are labeled as Q_H and Q_{SO_2} respectively. The variation of charge with SO₂ concentration is shown in Figure 3. It appears that the three highest concentrations produce approximately the same degradation; comparable voltage drops occur. This is consistent with the corresponding charges shown in Figure 3. The total amount SO₂ injected in each run is more than 1000 times the amount of SO₂ that would poison the entire catalyst surface. We have not determined the fate of the excess SO₂. Some of the impurity may be absorbed by the carbonaceous materials in the hardware (gas diffusion layers and graphite flow fields). Reaction of SO₂ with the water generated at the cathode (and also from air humidification), forming H₂SO₃, is also possible.

As suggested above, the presence of water at the cathode has an influence on the effect of SO₂ on performance. Figure 4 shows performance of a cathode with three air compositions. Performance degradation due to SO₂ is clearly more severe if the air is dry. Gas chromatograph analysis was performed on the humidified air stream before and after the fuel cell but the large concentration of H₂O that emits from the column greatly overwhelms/overlaps the small amount of SO₂ emitting from the column.

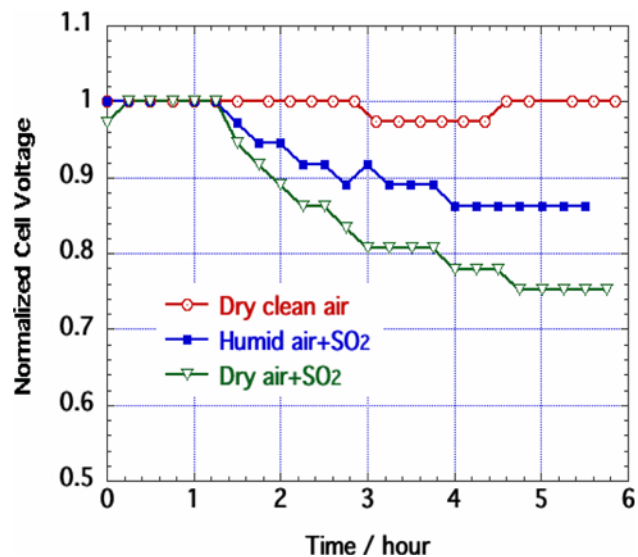


Figure 4. Effect of 1.5 ppm SO₂ on Performance with Humidified and Dry Air at 0.6 A/cm² constant Current (Anode and cathode loadings (mg Pt/cm²): 0.21 and 0.22 respectively. Cell operating on dry clean air did not experience performance losses.)

The severity of Pt-catalyst poisoning with SO₂ is clear from Figure 1. The poisoning is irreversible because of the strong affinity of sulfur with the metal. This means that further FC operation on neat air does not clean the catalyst surface (as it does with CO poisoning). Fuel containing sulfur impurities, such as H₂S, also poisons the catalyst irreversibly. The most convenient approach to dealing with this problem is to avoid the access of these impurities to the cell by using proper filters and/or sorbents [5a]. There remains, however, need for a contingency mechanism to remedy possible electrode contamination. Here we describe a simple and inexpensive procedure for *in-situ* reactivation of sulfur-poisoned Pt-catalysts [7]. The method consists of applying a power pulse using a low-power external power supply across the FC electrodes. Because, we are dealing with adsorbed species on the catalyst surface (usually a monolayer of molecules) the total amount of electrical charge for the electrochemical desorption of these species is small. Therefore, the power requirements are also small. A short voltage/current pulse is enough for cleaning the contaminated catalyst surface. Figure 5 shows an application of the method for a severely SO₂-

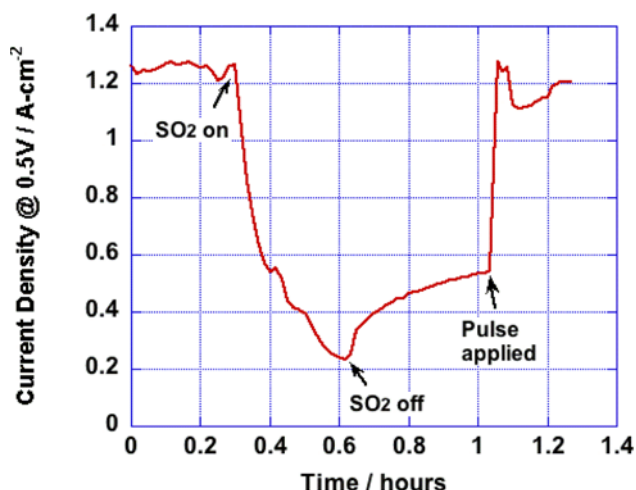


Figure 5. Cleaning a Cathode Poisoned with 10 ppm SO₂ at 80 °C (A 1.4 volt pulse was applied with an external power supply for 5 seconds. Anode and cathode loadings in mg Pt/cm²: 0.18 and 0.22 respectively. Cell size: 5 cm².)

contaminated cathode. Cell operation was momentarily interrupted and a 1.4 volt pulse was applied across the electrodes for 5 seconds (positive terminal connected to the cathode). The recovery of the FC performance was quite fast and the cell current practically returned to the original value recorded prior to poisoning. Figure 6 illustrates the procedure for H₂S-contaminated anode. In this case, before applying the pulse, the reactant's flows were interrupted but the cell was kept on. This allows most of the residual fuel to be consumed, leaving only the chemisorbed electro-active species on the Pt catalyst to be electro-oxidized by the external pulse. In this case, the power supply positive terminal was connected to the anode. The recovery of the FC performance was quite fast and the cell current practically returned to 95 % of original value recorded prior to poisoning.

We also tested the effects of NaCl on FC performance [5b]. This salt (from ocean mists and road de-icer) may contaminate the cathode air supply. The presence of NaCl at the electrode decreases its performance. The performance loss is mostly due to a decrease of protonic conductivity as a consequence of exchange of H⁺ by Na⁺ at the catalyst layer and at the membrane. Large concentrations of the salt also decreased the hydrophobicity of the gas diffusion layer, increased

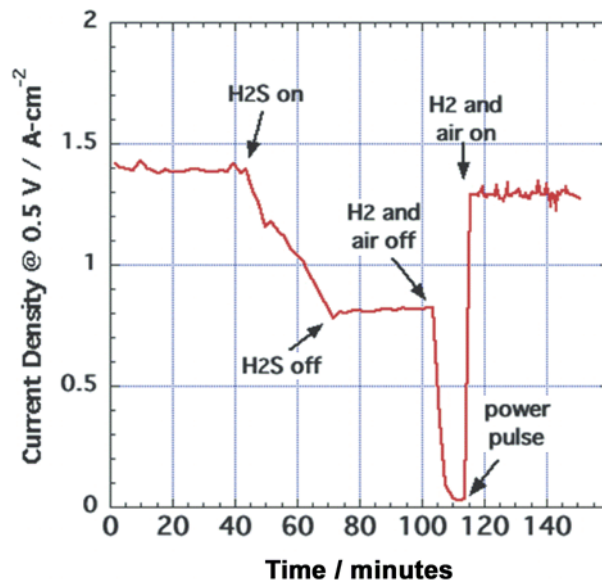


Figure 6. Cleaning an Anode Poisoned with 5 ppm H₂S at 80 °C (A 1.4 volt pulse was applied with an external power supply for 20 seconds. Loadings: 0.2 mg Pt/cm² at each electrode. Cell size: 5 cm².)

the volume of liquid water present and thus decreased oxygen transport to the electrocatalyst at high current densities. Unexpectedly, Cl⁻ does not appear to poison the catalyst surface as revealed by CV measurements.

Conclusions

- The SO₂ threshold poisoning level is lower than 250 ppb but larger than 100 ppb.
- The SO₂ degrading effect is more severe if the cell operates with dry air.
- Electrode Pt-catalysts can be reactivated from sulfur poisoning using a voltage pulse with an external power supply.
- The degrading effect of NaCl is mostly due to the decrease of protonic conductivity produced by the ionic exchange of H⁺ by Na⁺.

Special Recognitions & Awards/Patents Issued

1. F. Uribe and T. Zawodzinski; "Fuel cell anode for CO tolerance". U.S. Patent No. 6,818,341. Nov. 16, 2004.
2. F. Uribe and T. Rockward, 104929 Provisional Patent Application #97B96.

FY 2005 Publications/Presentations

1. P. Adcock, S. Pacheco, K. Norman, and F. Uribe, "Transition Metal Oxides as Reconfigured Fuel Cell Anode Catalysts for Improved CO Tolerance: Polarization Data," *J. Electrochem. Soc.*, 152, A459-A466 (2005).
2. J. Wang, F. Uribe and R. Adzic, "A Simple Semi-Analytic Method for Analyzing Fuel Cell Polarization Curves," Second International Conference on Polymer Batteries and Fuel Cells Symposium, the PBFC-2 Meeting The Electrochemical Society, Las Vegas, Nevada. June 12 -17, 2005. Abstract #203.
3. T. Rockward and F. Uribe, "Cleaning PEMFC Pt-Electrodes Poisoned with Adsorbed S-Species," 208th Meeting of The Electrochemical Society, Los Angeles, CA. October, 18, 2005.
4. M. Mikkola, T. Rockward, B. Pivovar and F. Uribe, "The Effect of NaCl in Cathode Air Stream on PEMFC Performance," submitted to: *Fuel Cells - From Fundamentals to Applications* journal. 2005.

References

1. F. A. Uribe, S. Gottesfeld, and T. A. Zawodzinski Jr., *J. Electrochem. Soc.* 149, A293 (2002).
2. F. Uribe and T. Zawodzinski, Jr., 200th Meeting of The Electrochemistry Society, San Francisco, CA, September 2001. Abstract 339.
3. (a) H. Soto, W. Lee, J. Van Zee, and M. Murthy, *Electrochemical and Solid-State Letters*; July 2003; vol.6, no.7, p.A133-5. (b) Mohtadi, R; Lee, WK; Cowan, S; Van Zee, JW; Murthy, M. *Electrochemical and Solid-State Letters*; Dec. 2003; vol.6, no.12, p.A272.
4. J. M. Moore, P. L. Adcock, J. B. Lakeman and G. O. Mepsted. *J. Power Sources*, 85 (2 000) 254.
5. (a) F. Uribe, J. Valerio and T. Rockward and E. Stenersen. 205th Meeting of The Electrochemistry Society, San Antonio, TX, May 2004. Abstract 332. (b) M. Mikkola, T. Rockward, E. Stenersen and F. Uribe. 205th Meeting of The Electrochemistry Society, San Antonio, TX, May 2004. Abstract 331.
6. R. Mohtadi, W. Lee, and J. Van Zee. *Journal of Power Sources*, 2004, 138, no.1-2, p.216-225.
7. F. Uribe and T. Rockward, 104929 Provisional Patent Application #97B96.